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(57) 【要約】

【目的】 導電材料と高分子固体電解質の複合化による導電材料／高分子固体電解質複合膜の製造方法に関する。

【構成】 導電材料表面に、分子内に $-CH_2-CH_2-O-$ で示されるエチレンオキシド構造を有する液状低分子有機シリコン化合物とリチウム支持電解質の混合物の層を形成させた後、あるいは予め前記混合物を含浸させた導電材料表面に前記混合物の層を形成させた後、プラズマによって前記混合物を重合させることを特徴とする導電材料／高分子固体電解質複合膜の製造方法。

【効果】 重合開始剤や架橋剤が不要であり、膜質が均一で導電材料と高分子固体電解質との密着性がよい高分子固体電解質膜を得ることができる。

【特許請求の範囲】

【請求項1】 導電材料表面に、分子内に $-CH_2-CH_2-O-$ で示されるエチレンオキシド構造を有する液状低分子有機シリコン化合物とリチウム支持電解質の混合物の層を形成させた後、プラズマによって前記混合物を重合させることを特徴とする導電材料／高分子固体電解質複合膜の製造方法。

【請求項2】 予め分子内に $-CH_2-CH_2-O-$ で

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(57) [Abstract]

[Objective] It regards manufacturing method of electrically conductive material / polymeric solid electrolyte composite membrane due to composite making of electrically conductive material and the polymeric solid electrolyte.

[Constitution] In electrically conductive material surface, layer of blend of liquid low molecular weight organosilicon compound and lithium supporting electrolyte which possess ethylene oxide structure which in intramolecular is shown with  $-CH_2-CH_2-O-$  after forming, or manufacturing method of electrically conductive material / polymeric solid electrolyte composite membrane which designates that the aforementioned blend is polymerized to electrically conductive material surface which beforehand impregnates aforementioned blend layer of aforementioned blend after forming, with plasma as feature.

[Effect(s)] Polymerization initiator and crosslinking agent are unnecessary, film quality is uniform and the polymeric solid electrolyte membrane where conformity of electrically conductive material and polymeric solid electrolyte is good can be acquired.

[Claim(s)]

[Claim 1] Manufacturing method of electrically conductive material / polymeric solid electrolyte composite membrane which designates that aforementioned blend is polymerized to electrically conductive material surface, layer of blend of liquid low molecular weight organosilicon compound and the lithium supporting electrolyte which possess ethylene oxide structure which in intramolecular is shown with the  $-CH_2-CH_2-O-$  after forming, with plasma as feature.

[Claim 2] Manufacturing method of electrically conductive m

示されるエチレンオキシド構造を有する液状低分子有機シリコン化合物とリチウム支持電解質の混合物を含浸させた導電材料表面に、分子内に $-CH_2-CH_2-O-$ で示されるエチレンオキシド構造を有する液状低分子有機シリコン化合物とリチウム支持電解質の混合物の層を形成させた後、プラズマによって前記混合物を重合させることを特徴とする導電材料／高分子固体電解質複合膜の製造方法。

aterial / polymeric solid electrolyte composite membrane which designates that aforementioned blend is polymerized to electrically conductive material surface which impregnates blend of liquid low molecular weight organosilicon compound and lithium supporting electrolyte which possess ethylene oxide structure which in intramolecular is shown beforehand with  $-CH_2-CH_2-O-$ , layer of blend of liquid low molecular weight organosilicon compound and the lithium supporting electrolyte which possess ethylene oxide structure which in intramolecular is shown with the  $-CH_2-CH_2-O-$  after forming, with plasma as feature.

#### 【発明の詳細な説明】

#### [Description of the Invention]

##### 【0001】

##### [0001]

【産業上の利用分野】本発明は導電材料と高分子固体電解質の複合化方法に関し、導電材料の酸化・還元機能を利用した電気化学素子（例えば、リチウム二次電池、エレクトロクロミック素子等）に適用される導電材料／高分子固体電解質複合膜の製造方法に関する。

【Field of Industrial Application】It regards manufacturing method of electrically conductive material / polymeric solid electrolyte composite membrane which is applied to electrochemical element (Such as for example lithium secondary battery and electrochromic element) where this invention regards composite making method of electrically conductive material and polymeric solid electrolyte, utilizes the oxidation and reduction function of electrically conductive material.

##### 【0002】

##### [0002]

【従来の技術】近年、エネルギー・環境問題を背景に従来の二次電池（例えば、鉛電池、Ni / Cd電池等）よりも高いエネルギー密度を有するリチウム二次電池が注目されており、国家プロジェクトをはじめ鋭意研究が行われている。このリチウム二次電池の課題の一つとして液体の電解質を用いることによる潜在的な液漏れや揮発の問題があげられる。このことは電池セル全体の軽量化・コンパクト化にも影響を及ぼしており、このような背景から、将来的には高分子固体電解質を用いた全固体型リチウム二次電池の開発が要請されている。

【Prior Art】Recently, energy \* environmental problem lithium secondary battery which possesses high energy density in comparison with conventional secondary battery (Such as for example lead battery and Ni / Cd battery) is observed by background, diligent research is done including national project. It can increase problem of potential liquid leak and volatilization due to using the electrolyte of liquid as one of problem of this lithium secondary battery. this has exerted influence to also light weight \* compaction of battery cell entirety, from this kind of background, development of completely solid type lithium secondary battery which uses polymeric solid electrolyte is requested to future.

【0003】この全固体型リチウム二次電池を製造するにあたっては、従来、導電材料と高分子固体電解質膜の複合化を主に以下の方法で行われていた。

【0003】When this completely solid type lithium secondary battery is produced, until recently, composite making of electrically conductive material and polymeric solid electrolyte membrane was done mainly with method below.

(1) 予め合成された高分子固体電解質材料とリチウム支持電解質を適当な有機溶媒に混合・溶解させて溶液を作製し、当該溶液を導電材料上にキャスト又はスピナーによりコーティングして乾燥させることにより、上記複合膜を得る方法。

(1) Mixed \* melting polymeric solid electrolyte material and lithium supporting electrolyte which are synthesized beforehand in suitable organic solvent, method which obtains above-mentioned composite membrane by producing solution, coating doing on electrically conductive material with the cast or spinner, it dries this said solution.

(2) 高分子固体電解質の原料となる低分子材料（以下、単に原料低分子と略する）とリチウム支持電解質の混合体を導電材料上にコートし、重合開始剤を添加して低分子材料を重合させて固体化し、上記複合膜を得る方法。

(3) 原料低分子とリチウム支持電解質の混合体を導電材料上にコートし、低分子材料に架橋反応を行わせて固体化し、上記複合膜を得る方法。

#### 【0004】

【発明が解決しようとする課題】上記の(1)～(3)までの従来技術は導電材料との複合化に際して、それぞれ以下の課題を有する。

【0005】前記(1)の従来技術では、高分子固体電解質の分子量が高いと溶液の粘度が高くなり、成膜時の薄膜化が困難である。また、溶液中の溶媒を揮発させて乾燥する際に膜厚が不均一になりやすく、得られる高分子固体電解質膜にピンホールが生成しやすい。また、導電材料が導電性高分子など多孔質材料である場合、高粘度の高分子固体電解質を導電材料中へ浸透させることは困難であるため、導電材料／高分子固体電解質膜界面の抵抗成分が大きくなり、電池系としての内部抵抗が大きくなる。逆に高分子固体電解質の分子量が低いと、成膜性が向上し薄膜化も容易になるが、機械的強度が弱くなり、対向電極（リチウム二次電池の場合、負極）と接触させた場合、電極間短絡を生じやすい。

【0006】前記(2)及び(3)の従来技術では、高分子固体電解質膜の合成に重合開始剤や架橋源を必要とする。高分子を架橋反応させる方法として架橋剤を用いる方法があるが、原料低分子膜への架橋剤濃度の制御及び原料低分子膜全面への均一配合は困難である。また、架橋源として紫外光を用いる方法（T. Kabata et al., Polymers for Advanced Technologies, 4, 205(1993)）では均一な成膜が容易であるが、原料低分子の分子構造に光反応性の官能基を導入する工程を必要とし、導電材料が遮光性及び吸光性を有する材料である場合（例：導電

(2) Low molecular weight material which becomes starting material of polymeric solid electrolyte (Below, starting material low molecular weight you abbreviate simply.) with coating doing the mixture of lithium supporting electrolyte on electrically conductive material, adding polymerization initiator and polymerizing the low molecular weight material method which solidification it does, obtains the above-mentioned composite membrane.

(3) Method where coating it does mixture of starting material low molecular weight and lithium supporting electrolyte on electrically conductive material, makes crosslinking reaction low molecular weight material do and solidification does, obtains the above-mentioned composite membrane.

#### [0004]

[Problems to be Solved by the Invention] Prior Art to above-mentioned (1) to (3) has problem below each one in case of composite making of electrically conductive material.

[0005] With Prior Art of aforementioned (1), when molecular weight of polymeric solid electrolyte is high, viscosity of solution becomes high, making thin film at time of the film formation is difficult. In addition, volatilization doing solvent in solution, when drying, the film thickness is easy to become nonuniform, pinhole is easy to form in polymeric solid electrolyte membrane which is acquired. In addition, when electrically conductive material such as conductive polymer it is a porous material, polymeric solid electrolyte of the high viscosity as for permeating to in electrically conductive material because it is difficult, the resistance component of electrically conductive material / polymeric solid electrolyte membrane interface becomes large, internal resistance as battery system becomes large. When molecular weight of polymeric solid electrolyte is low conversely, film forming behavior improves and also making thin film becomes easy, but mechanical strength becomes weak, when the counter electrode (In case of lithium secondary battery, negative electrode) with it contacted, is easy to cause short circuit between the electrode.

[0006] With Prior Art of aforementioned (2) and (3), polymerization initiator and crosslinking source are needed in synthesis of polymeric solid electrolyte film. There is a method which uses crosslinking agent crosslinking reaction is done polymer as the method which, but uniform blending to control and starting material low molecular weight film entire surface of crosslinking agent concentration to starting material low molecular weight film is difficult. In addition, with method {T. Kabata et al., polymers for Advanced Technologies, 4, 205(1993)} which uses ultraviolet light as crosslinking source

性高分子のような有色材料)には適用でき、その他、 $\gamma$ 線を照射して架橋した高分子固体電解質を得る方法 [MacCallum et al., Solid State Ionics, 11, 307(1984)] も提案されているが、大面積化が困難であり、 $^{60}\text{Co}$  のような放射性的  $\gamma$  線の発生源を必要とする。

【0007】本発明は上記技術水準に鑑み、従来法におけるような不具合を解消した導電材料/高分子固体電解質複合膜の製造方法を提供しようとするものである。

【0008】

【課題を解決するための手段】本発明は(1)導電材料表面に、分子内に $-\text{CH}_2-\text{CH}_2-\text{O}-$ で示されるエチレンオキシド構造を有する液状低分子有機シリコン化合物とリチウム支持電解質の混合物の層を形成させた後、プラズマによって前記混合物を重合させることを特徴とする導電材料/高分子固体電解質複合膜の製造方法及び(2)予め分子内に $-\text{CH}_2-\text{CH}_2-\text{O}-$ で示されるエチレンオキシド構造を有する液状低分子有機シリコン化合物とリチウム支持電解質の混合物を含浸させた導電材料表面に、分子内に $-\text{CH}_2-\text{CH}_2-\text{O}-$ で示されるエチレンオキシド構造を有する液状低分子有機シリコン化合物とリチウム支持電解質の混合物の層を形成させた後、プラズマによって前記混合物を重合させることを特徴とする導電材料/高分子固体電解質複合膜の製造方法である。

【0009】すなわち、本発明では液状の原料低分子(分子内に $-\text{CH}_2-\text{CH}_2-\text{O}-$ で示されるエチレンオキシド構造を有する液状低分子有機シリコン化合物)にリチウム支持電解質を混合させた液(以下、原料低分子溶液という)を、予め原料低分子混合液を含浸させた又は含浸させていない導電材料の表面に滴下、塗布などの方法により付着させて原料低分子混合液の層を形成させた後、低真空下でグロー放電プラズマを作用させて当該混合物を重合させて高分子固体電解質膜(以下、高分子固体電解質とは、原料低分子とリチウム支持電解質との混合物を重合させたものを意味する)を合成して導電材料/高分子固体電解質複合膜を得ようとするものである。

the uniform film formation is enabled by step which introduces functional group of photoreactivity into molecular structure of starting material low molecular weight is needed, when it is a material where the electrically conductive material has light blocking and light-absorbing it cannot apply to (Like example: conductive polymer is colored material). In addition, irradiating  $\gamma$ -ray, also method [MacCallum et al., Solid State Ionics, 11, 307(1984)] which obtains the polymeric solid electrolyte which crosslinking is done is proposed, but source of  $\gamma$ -ray of radioactivity where surface area enlarging is difficult, like  $^{60}\text{Co}$  is needed.

[0007] It is something which, it tries you will consider this invention to the above-mentioned technology level, to offer manufacturing method of electrically conductive material / polymeric solid electrolyte composite membrane which cancels the kind of disadvantage in prior art method.

[0008]

[Means to Solve the Problems] As for this invention to (1) electrically conductive material surface, Layer of blend of liquid low molecular weight organosilicon compound and lithium supporting electrolyte which possess ethylene oxide structure which in intramolecular is shown with  $-\text{CH}_2-\text{CH}_2-\text{O}-$  after formation, manufacturing method of electrically conductive material / polymeric solid electrolyte composite membrane which designates that aforementioned blend is polymerized with plasma as feature and (2) impregnates blend of liquid low molecular weight organosilicon compound and lithium supporting electrolyte which possess ethylene oxide structure which beforehand in the intramolecular is shown with  $-\text{CH}_2-\text{CH}_2-\text{O}-$  to electrically conductive material surface which, It is a manufacturing method of electrically conductive material / polymeric solid electrolyte composite membrane which designates that aforementioned blend is polymerized layer of blend of liquid low molecular weight organosilicon compound and lithium supporting electrolyte which possess ethylene oxide structure which in intramolecular is shown with  $-\text{CH}_2-\text{CH}_2-\text{O}-$  after forming, with plasma as feature.

[0009] With namely, this invention starting material low molecular weight mixed solution was impregnated beforehand or to drip the liquid (Below, starting material low molecular weight solution you call) which mixes lithium supporting electrolyte to starting material low molecular weight (It possesses ethylene oxide structure which in intramolecular is shown with  $-\text{CH}_2-\text{CH}_2-\text{O}-$  the liquid low molecular weight organosilicon compound) of liquid, to the surface of electrically conductive material which has not been impregnated, depositing with the application or other method, layer of starting material low molecular weight mixed solution glow discharge plasma operating after forming, and under low vacuum polymerizing

this said blend, synthesizing the polymeric solid electrolyte film (Below, polymeric solid electrolyte, those which polymerized blend of the starting material low molecular weight and lithium supporting electrolyte are meant.), it is something which it tries to obtain electrically conductive material / polymeric solid electrolyte composite membrane.

【0010】適用可能な導電材料にはポリアニリン、ポリチオフェン、ポリピロール、ポリアセン、ポリアセチレンなどの導電性高分子の他、二酸化マンガ、二硫化チタン、コバルト酸リチウムなど無機材料などがあげられる。これらの導電材料は化学重合法、電解重合法及び気相重合法等いずれの方法で合成されたものでもよい。

[0010] Other than polyaniline, polythiophene, polypyrrole, polyacene and polyacetylene or other conductive polymer, you can list to applicable electrically conductive material inorganic material etc such as manganese dioxide, titanium disulfide and lithium cobaltate. These electrically conductive material may be something which such as chemical polymerization method with any method, electrolytic polymerization method and vapor phase polymerization method is synthesized.

【0011】本発明において、高分子固体電解質の原料低分子としては、分子構造中にリチウムイオン伝導に寄与するエチレンオキシド構造（ $-C_2H_4-O-$ ）を有し、プラズマ重合時の圧力下（約1～2 Torr）での沸点が室温程度（約20℃）以上であれば、原理的にどのような低分子でも利用可能である。このような化合物の中で、特に低分子の分子構造にシリコンを含むものは、プラズマに対する耐エッチング性がよく、高分子化させることが容易である。そのため、本発明では原料として分子内に $-CH_2-CH_2-O-$ で表されるエチレンオキシド構造を少なくとも1個有する、室温・常圧の状態で液状の低分子有機シリコン系化合物を使用する。また、真空槽内の原料低分子の気化を防ぐため、なるべく高沸点（低蒸気圧）の原料を選択することが望ましい。例えば以下の化合物をあげることができる。

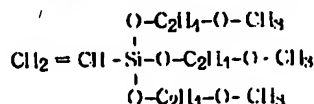
[0011] Regarding to this invention, if it possesses ethylene oxide structure ( $-C_2H_4-O-$ ) which contributes to the lithium ion conduction in molecular structure as starting material low molecular weight of polymeric solid electrolyte, and boiling point with the (Approximately 1 to 2 Torr) under pressure at time of plasma polymerization is above room temperature extent (Approximately 20 °C), in principle it is a useable any kind of low molecular weight. In this kind of compound, as for those which include silicon in the molecular structure of especially low molecular weight, etching resistance for plasma good, what the polymerization is done easy. Because of that, with this invention at least one it possesses ethylene oxide structure which in intramolecular is displayed with  $-CH_2-CH_2-O-$  as starting material, low molecular weight organosilicon compound of liquid is used with state of room temperature \* ambient pressure. In addition, in order to prevent evaporation of starting material low molecular weight inside the vacuum chamber, it is desirable if possible to select starting material of the high boiling point (low vapor pressure). It is possible to increase compound below for example.

【0012】

【化1】

トリス(2-メトキシエトキシ)ビニルシラン

沸点：115～117℃ (2 Torr)



[0012]

[Chemical Formula 1]

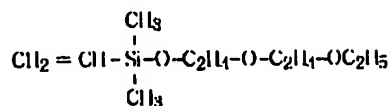
【0013】

[0013]

【化2】

ジメチル-2,1,2-エトキシエトキシ-エトキシ-ビニルシラン

沸点: 75~76°C (4 Torr)

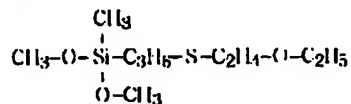


【0014】

**【化3】**

ジメトキシ・3(2エトキシエチルチオフロビル)メチルシラン

沸点: 125~128℃ 1 Torr

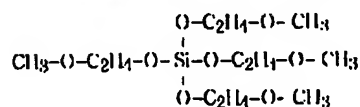


**【0015】**

【化 4】

テトラキス(2-メトキシエトキシ)シラン

沸点: 140~141℃ (1 Torr)

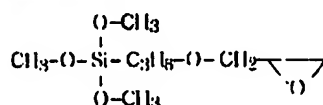


**【0016】**

【化 5】

### 3 グリシドキシブロピルトリメチルシラン

沸点: 119~121°C 21orr.

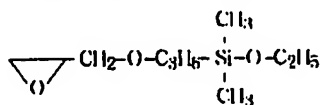


**[0017]**

【化6】

ジメチルエトキシ-3'-グリシドキシプロピルシラン

沸点: 99~100°C (3 Torr)



**[Chemical Formula 2]**

[0014]

**[Chemical Formula 3]**

[0015]

**[Chemical Formula 4]**

[0016]

**[Chemical Formula 5]**

[0017]

**[Chemical Formula 6]**

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【0018】また、リチウム支持電解質としては過塩素酸リチウム ( $\text{LiClO}_4$ )、四フッ化ホウ素酸リチウム ( $\text{LiBF}_4$ )、六フッ化リン酸リチウム ( $\text{LiPF}_6$ )、六フッ化ヒ素酸リチウム ( $\text{LiAsF}_6$ )、トリフルオロメタンスルホン酸リチウム ( $\text{LiCF}_3\text{SO}_3$ )、チオシアン酸リチウム ( $\text{LiSCN}$ ) などのリチウム金属塩を用いることができる。

【0019】導電材料上に原料低分子混合液層を形成させる方法としては、原料低分子混合液を、予め原料低分子混合液を含浸させた又は含浸させていない導電材料表面に塗布したりマイクロシリジンなどで一定量ずつ滴下するなどの手段により表面に原料低分子混合液の層を形成させる方法があげられるが、導電材料が微細な空孔を有する多孔質構造である場合、上記原料低分子混合液を含浸、付着後、真空デシケータ内で脱気させるか、逆に脱気後原料低分子／リチウム支持電解質混合物を含浸、付着させるなどの方法により導電材料中へ十分浸透させる工夫を必要とする。

【0020】また、本複合体の性能（イオン伝導性）を再現性良く管理するためには、上述した導電材料中への原料低分子混合液の十分な浸透と併せて、導電材料上の固体電解質層の厚みを制御することが重要である。このためには、原料低分子混合液を含ませた導電材料から原料低分子混合液が漏れず、また、表面上に形成させる原料低分子混合液層の液が流れ出さないような適当な構造の支持枠中に導電材料を収め、導電材料上の余分な原料低分子混合液を除去した後、所定量の原料低分子混合液を滴下する等の工夫が必要である。

【0021】本発明の方法においては、このようにして作製した導電材料／低分子混合液の複合体に、真空中でグロー放電プラズマを作用させて原料低分子重合させ、高分子固体電解質複合体とする。

【0022】本発明で使用するプラズマ重合装置につい

[0018] In addition, lithium perchlorate ( $\text{LiClO}_4$ ), boron tetrafluoride acid lithium ( $\text{LiBF}_4$ ), lithium hexafluorophosphate ( $\text{LiPF}_6$ ), hexafluoro arsenic acid lithium ( $\text{LiAsF}_6$ ), lithium trifluoromethane sulfonate ( $\text{LiCF}_3\text{SO}_3$ ) and the lithium thiocyanate ( $\text{LiSCN}$ ) or other lithium metal salt can be used as lithium supporting electrolyte.

[0019] Forms starting material low molecular weight mixed solution layer on electrically conductive material as method which, starting material low molecular weight mixed solution, Beforehand, you can list method starting material low molecular weight mixed solution was impregnated or applying to electrically conductive material surface which has not been impregnated and/or forming the layer of starting material low molecular weight mixed solution in surface with at a time constant amount or other means which with such as micro titration is dripped but, When it is a porous structure where electrically conductive material has microscopic void, it impregnates the above-mentioned starting material low molecular weight mixed solution, outgassing does after depositing, or and inside vacuum dessicator impregnates starting material low molecular weight / lithium supporting electrolyte blend after outgassing conversely, the fully it needs device which permeates to in electrically conductive material with or other method which deposits.

[0020] In addition, in order reproducibility to manage performance (ionic conductivity) of this composite well, adjusting to sufficient permeation of starting material low molecular weight mixed solution to in electrically conductive material which description above is done, it is important to control the thickness of solid electrolyte layer on electrically conductive material. For this, starting material low molecular weight mixed solution does not leak from electrically conductive material which makes starting material low molecular weight mixed solution include, in addition, after liquid of starting material low molecular weight mixed solution layer which is formed on surface flows out and is to supply electrically conductive material, removing the excess starting material low molecular weight mixed solution on electrically conductive material in support frame of suitable construction, or other device which drips starting material low molecular weight mixed solution of predetermined amount is necessary.

[0021] Regarding to method of this invention, in composite of electrically conductive material / low molecular weight mixed solution which it produces in this way, glow discharge plasma operating under vacuum, the starting material low molecular weight polymerizing, it makes polymeric solid electrolyte composite membrane.

[0022] Concerning plasma polymerization equipment which is



て、図1を例として説明する。ベルジャー真空槽1内に基板ホルダ2と放電電極3を設けた構造である。放電電極3は放電電源4に接続されており、真空槽1は油回転ポンプもしくはメカニカルブースターポンプなどの排気系5に配管で接続されている。また、真空槽1内の圧力はピラニ真空計などの圧力計6により観測できるものとする。導電材料/原料低分子混合液複合膜7は基板ホルダ2上にセットされる。このとき原料低分子混合液の流れ出しによる膜厚の不均一化を防ぐため、基板ホルダ2は水平に設置し、原料低分子の真空槽1内での蒸発を防ぐために冷却水により基板ホルダ2自体を冷却できる構造とすることが好ましい。放電電極3はプラズマ重合を成膜面全体に均一に行うため基板ホルダ2に平行に配し、電極面積は成膜面積と同程度か若干大きいこととする。放電電源4は電極3間をグロー放電可能な出力電圧(約300~500V)及び出力(放電電極の単位面積当り最大1mA/cm<sup>2</sup>の電流密度)を有していれば、直流の他、商用周波数、ラジオ波周波数(13.56MHz)等原理的にいずれの周波数帯域のものでもよい。

【0023】真空槽1内の雰囲気は安定したグロー放電を得るため、不活性ガス供給源8よりアルゴン、ヘリウムなどの希ガスを真空槽1内に導入することが好ましい。また、真空槽1内の圧力が過度に低いと原料低分子が真空槽1内で蒸発するため、安定なグロー放電が発生可能な範囲(1~2Torr)に保持することが望ましい。

【0024】固体電解質層の機械的強度は真空槽内の放電電力及び放電時間により調整が可能である。すなわち、放電電力を大きくするか放電時間を長くすることによって固体電解質層の重合膜の機械的強度が上がる。しかし、過度に放電電力が大きい場合あるいは重合時間が長い場合、固体電解質層の機械的強度が上がる反面、イオン伝導度が著しく低下するため、固体電解質層の機械的強度の許容範囲内(リチウム電池の場合、負極との接触に耐え得る程度)で放電電力を極力低くするか、または放電時間を短くすることが望ましい。

【0025】

sed with this invention, you explain the Figure 1 as example. It is a structure which provides substrate holder 2 and discharge electrode 3 inside vacuum chamber 1 of bell jar shape. discharge electrode 3 is connected by discharge power supply 4. vacuum chamber 1 is connected to oil rotary pump or mechanical booster pump or other exhaust system 5 with pipe. In addition, pressure inside vacuum chamber 1 we can observe with Pirani- vacuum gauge or other pressure gauge 6. electrically conductive material / starting material low molecular weight mixed solution composite membrane 7 is set on substrate holder 2. This time flowing out of starting material low molecular weight mixed solution it dies and in order to prevent the becoming nonuniform of film thickness which depends, it installs substrate holder 2 in the horizontal, it is desirable in order to prevent evaporation inside the vacuum chamber 1 of starting material low molecular weight to make structure which can cool substrate holder 2 itself with the cooling water. In order in film forming surface entirety to do plasma polymerization in uniform, it allots the discharge electrode 3 parallel to substrate holder 2, electrode surface area film forming surface product same extent makes somewhat large thing. Discharge power supply 4 if between electrode 3 it has possessed glow discharge possible output voltage (Approximately 300 to 500V) and output (current density of per unit surface area maximum 1 mA/cm<sup>2</sup> of discharge electrode), other than direct current, is good to principle such as commercial frequency and radiowave frequency (13.56 MHz) those of any high frequency band.

[0023] As for atmosphere inside vacuum chamber 1 in order to obtain glow discharge which is stabilized, it is desirable from inert gas source 8 to introduce argon and helium or other rare gas into vacuum chamber 1. In addition, when pressure inside vacuum chamber 1 is low excessively, the starting material low molecular weight inside vacuum chamber 1, in order to evaporate, stability it is desirable for glow discharge to keep in generatable range (1 to 2 Torr).

[0024] As for mechanical strength of solid electrolyte layer adjustment is possible with discharge power and discharge time inside vacuum chamber. namely, discharge power is enlarged, mechanical strength of polymer film of solid electrolyte layer rises by making discharge time long. But, when discharge power is large excessively or when polymerization time is long, while mechanical strength of solid electrolyte layer rises, because ionic conductivity decreases considerably, with (In case of lithium battery, it can withstand contact with negative electrode to the extent) inside tolerance of mechanical strength of solid electrolyte layer, the discharge power is made forcible low or it is desirable to make the discharge time short.

[0025]

【作用】本発明では高分子固体電解質の原料となる低分子をリチウム支持電解質と混合後、導電材料上に複合化させるため、導電材料と高分子固体電解質との密着性（機械的強度及び電気的強度）がよい。この作用は導電材料が導電性高分子等の多孔質材料の場合、原料低分子混合液の導電材料中への浸透がよいため両者の界面付近に混合層が形成されるので、特に有効である。この効果は原料低分子混合液の層を形成させるに先立って導電材料に原料低分子混合液を含浸させておくことによってさらに高めることができる。

【0026】また、プラズマを原料低分子の重合源及び架橋源として用いるため、重合開始剤や架橋剤が不要であると同時に膜面上で膜質（化学構造、分子量、架橋密度、塩濃度等）の均一な高分子固体電解質膜を得ることができる。

【0027】

【実施例】以下、実施例に基づいて本発明の方法をさらに具体的に説明する。

#### (実施例 1)

(1) 過塩素酸リチウム（リチウム支持電解質）をトリス（2-メトキシエトキシ）ビニルシラン（原料低分子）中に10重量%溶解させて原料低分子混合液を作製した。

(2) 化学重合法により作製したポリアニリン膜（直径3cm、厚さ1mm）を前記（1）の原料低分子混合液中に浸し、ポリアニリン膜中の微細な空隙中に（1）の原料低分子混合液を十分含浸させるため、真空デシケータ内で脱気した。1時間後、ポリアニリン膜からの発泡が認められなくなり、脱気が十分に行われたことを確認した。

【0028】（3）本実施例では、プラズマによって原料低分子混合液を固体化させる前に固体膜中に原料低分子混合液を含浸させ、更に固体膜上にも一定の厚みの混合液層を形成させるため、混合液の漏れ、流れだしを防止する必要がある。また、極めて反応性の高いリチウム金属を用いて電池系を構成するため、外気の水分や酸素

[Work or Operations of the Invention] In order with this invention low molecular weight which becomes starting material of polymer solid electrolyte composite making to do after lithium supporting electrolyte and mixture and on electrically conductive material, the conformity (mechanical strength and electrical strength) of electrically conductive material and polymeric solid electrolyte is good. Because as for at this action when electrically conductive material is conductive polymer or other porous material, because permeation to in electrically conductive material of starting material low molecular weight mixed solution is good, mixed layer is formed to interface vicinity of both, especially it is effective. This effect layer of starting material low molecular weight mixed solution is formed preceding, furthermore can raise by impregnating starting material low molecular weight mixed solution in electrically conductive material.

[0026] In addition, in order plasma to use, as polymerization source and crosslinking source of starting material low molecular weight when polymerization initiator and crosslinking agent are unnecessary, uniform polymeric solid electrolyte film of film quality (Such as chemical structure, molecular weight, crosslink density and salt concentration) can be acquired simultaneously on film surface.

[0027]

[Working Example(s)] Method of this invention furthermore is explained concretely below, on the basis of Working Example.

#### (Working Example 1)

(1) 10 weight% melting lithium perchlorate (lithium supporting electrolyte) in tris (2-methoxy ethoxy) vinyl silane (starting material low molecular weight), it produced starting material low molecular weight mixed solution.

(2) It soaked polyaniline film (diameter 3 cm and thickness 1 mm) which is produced with chemical polymerization method in starting material low molecular weight mixed solution of aforementioned (1), in order fully to impregnate starting material low molecular weight mixed solution of (1) in microscopic void in polyaniline film, outgassing it did inside the vacuum dessicator. After 1 hour, foaming from polyaniline film stopped being recognized, you verified that outgassing was done in fully.

[0028] (3) With this working example, solidification before doing starting material low molecular weight mixed solution, impregnating the starting material low molecular weight mixed solution in solid membrane with plasma, in order furthermore to form the mixed solution layer of fixed thickness even on solid membrane, a leak of mixed solution, it starts flowing,

から試料を保護する必要がある。以上の理由から、本実施例における導電材料／高分子固体電解質複合膜の作製及び性能評価には図2に示す評価セルを用いた。評価セルの構造は正極部（正極材料／高分子固体電解質複合膜21、正極カバー22、正極集電板23、及び角ガスケット24、以下セル正極部と総称する）と負極部（負極カバー27、負極集電板28、以下セル負極部と総称する）からなる。また、正極側及び負極側の端子（25及び29）はそれぞれ正極集電板23及び負極集電板28と電気的に導通している。

【0029】前記評価セル各部の材質は、正極カバー22及び負極カバー27がテフロン製、正極集電板23、正極側の端子25、負極集電板28及び負極側の端子29がステンレス製、角ガスケット24がシリコンゴム型である。

【0030】ポリアニリン膜を前記(1)の原料低分子混合液から引き揚げ、セル正極部にポリアニリン膜面が正極集電板23上に来るようにセットする。ここで原料低分子混合液がポリアニリン膜上に付着していると、正極上に形成する高分子固体電解質層の厚みを正確に制御することが困難であるため、脱脂綿で余分な原料低分子混合液を取り除いた後(1)と同一組成の原料低分子混合液をマイクロシリンジによってポリアニリン膜上に所定量滴下して所望の厚みの原料低分子液層を得ることとした。原料低分子混合液の滴下量とその厚みの関係は次式に従った。

$$(\text{滴下量}) = (\text{厚み}) \times (\text{正極材料の面積})$$

【0031】本実施例では、ポリアニリン膜の表面粗さとの対応から原料低分子液層の厚みを $20\mu\text{m}$ とした。ポリアニリン膜の面積は $7.1\text{cm}^2$ （直径 $3\text{cm}$ ）から、 $14\mu\text{l}$ の原料低分子混合液をポリアニリン膜上に滴下した。この状態において、セルの角ガスケット24と正極カバー22間からの原料低分子混合液の漏れは認

necessary to prevent it is. In addition, because battery system is formed making use of lithium metal where the reactivity is high, it is necessary to protect sample from the moisture or oxygen of external air. From reason above, test cell which is shown in Figure 2 was used to production and performance evaluation of electrically conductive material / polymeric solid electrolyte composite membrane in this working example. structure of test cell positive electrode part ( anode material / polymeric solid electrolyte composite membrane 21, positive electrode cover 22, positive electrode collector sheet 23, and angular gasket 24, the cell positive electrode part and generic below it does. ) with consists of negative electrode part ( cell negative electrode part and generic below negative electrode cover 27, negative electrode collector sheet 28 and it does. ). In addition, terminal (25 and 29) of positive electrode side and negative electrode side continuity has done in respective positive electrode collector sheet 23 and negative electrode collector sheet 28 and electrical.

[0029] As for material of aforementioned test cell section, positive electrode cover 22 and the negative electrode cover 27 terminal 25 of Teflon, positive electrode collector plate 23 and positive electrode side, terminal 29 of the negative electrode collector plate 28 and negative electrode side stainless steel and angular gasket 24 is silicone rubber make.

[0030] It pulls polyaniline film from starting material low molecular weight mixed solution of aforementioned (1) and fries, in order for polyaniline film aspect to come on positive electrode collector sheet 23 in cell positive electrode part, it sets. When here starting material low molecular weight mixed solution has deposited on polyaniline film, because it is difficult, to control thickness of polymeric solid electrolyte layer which is formed on the positive electrode accurately after removing excess starting material low molecular weight mixed solution with absorbent cotton, (1) with the predetermined amount dripping starting material low molecular weight mixed solution of same composition on polyaniline film with microsyringe, to obtain starting material low molecular weight liquid layer of desired thickness. You followed dropped amount of starting material low molecular weight mixed solution and relationship of thickness then next formula.

$$(\text{Dropped amount}) = (\text{thickness}) \times (\text{surface area of anode material})$$

[0031] With this working example, thickness of starting material low molecular weight liquid layer was designated as  $20\mu\text{m}$  from correspondence with surface roughness of polyaniline film. surface area of polyaniline film from  $7.1\text{cm}^2$  (diameter  $3\text{cm}$ ), dripped starting material low molecular weight mixed solution of  $14\mu\text{l}$  on polyaniline film. In this state,

められなかった。

【0032】(4) 前記(3)で得たポリアニリン/原料低分子混合液複合膜をセル正極部にセットされたままの状態、プラズマ重合装置内の基板ホルダーにセットした。基板ホルダーの下面には約5℃の冷却水を配管により循環させて、プラズマによる基板ホルダーの温度上昇に伴う原料低分子混合液の蒸発を防いだ。次に、アルゴンガスを30 cm<sup>3</sup>/min (at 25℃, 1 atm) の流量で流しながら真空槽内を圧力1 Torrまで排気後、周波数10 kHz、放電電力15 W (放電電極上の電流密度:  $2.6 \times 10^{-4}$  A/cm<sup>2</sup>) で2時間プラズマ重合させた。放電終了後、真空槽内を窒素ガスで大気圧まで戻し、セル正極部を取り出した。

【0033】(5) 得られた複合膜のプラズマ重合部分は柔軟な固体膜であり、セル正極部を傾けても複合膜からの液状物質の流れ出しや変形は認められなかった。また、赤外吸収分光法により重合膜の化学構造を評価したところ、原料低分子中に含まれていたエチレンオキシド構造が保持されていることが確認された。窒素ガス雰囲気にしたグローブボックス中で、セル正極部にセットされた複合膜上にリチウム箔(直径1 cm、厚さ0.3 mm、負極集電板28に導通)及び負極カバー27を重ねて、複合膜/リチウム箔複合体を得た。(以下、電池系と称する)セル内の電池系はセル正極部とセル負極部をボルト/ナットにより結合することによって外気と遮断され、セル正極部及び負極部に端子(25及び29)を取り付けて外部とセル内の導通を取り、充放電特性を評価したところ、電流密度0.01 mA/cm<sup>2</sup>の充放電サイクルで開放端電圧は3.3 Vであり、電池として機能することを確認した。

#### 【0034】(実施例2)

(1) トリフルオロメタンスルホン酸リチウムをジメチル-2-((2-エトキシエトキシ)エトキシ)ビニルシラン中に10重量%溶解させてリチウム支持電解質/原料低分子混合液を作製した。

(2) 化学重合法により作製した二酸化マンガング膜(直

angular gasket 24 of cell and blocking of starting material low molecular weight mixed solution from between positive electrode cover 22 were not recognized.

[0032] (4) Polyaniline / starting material low molecular weight mixed solution composite membrane which is acquired with aforementioned (3) with state while it was set to cell positive electrode part, was set to substrate holder inside plasma polymerization equipment. It prevented evaporation of starting material low molecular weight mixed solution which circulating due to the pipe, accompanies cooling water of approximately 5 °C temperature rise of the substrate holder due to plasma in bottom surface of substrate holder. While next, letting flow argon gas with flow of 30 cm<sup>3</sup> / min (at 25 °C, 1 atm), inside the vacuum chamber to pressure 1 Torr after exhaust, 2 hours plasma polymerization it did with the frequency 10 kHz, discharge power 15 W (current density :  $2.6 \times 10^{-4}$  A/cm<sup>2</sup> on discharge electrode). After discharge ending and inside vacuum chamber you reset to atmospheric pressure with nitrogen gas, removed cell positive electrode part.

[0033] (5) Plasma polymerization portion of composite membrane which it acquires it was a flexible solid membrane, cell positive electrode part tilted and liquid substance from composite membrane did to flow out and deformation was not recognized. In addition, when chemical structure of polymer film is appraised with infrared absorption spectroscopy, it was verified that ethylene oxide structure which is included in starting material low molecular weight is kept. In glovebox which is made nitrogen gas atmosphere, repeating lithium foil (In diameter 1 cm, thickness 0.3 mm and negative electrode collector sheet 28 continuity) and the negative electrode cover 27 on composite membrane which is set to cell positive electrode part, it acquired the composite membrane / lithium foil composite. battery system inside (Below, it names battery system.) cell external air and blocking was done by connecting cell positive electrode part and cell negative electrode part with bolt/nut installed terminal (25 and 29) in cell positive electrode part and negative electrode part took continuity inside outside and the cell, when charge-discharge characteristic is appraised, release end voltage was 3.3 V with the charge-discharge cycle of current density 0.0 mA/cm<sup>2</sup>, verified that it functions as battery.

#### [0034] (Working Example 2)

(1) 10 weight% melting lithium trifluoromethane sulfonate in dimethyl-2-((2-ethoxyethoxy)ethoxy)vinyl silane, it produced lithium supporting electrolyte / starting material low molecular weight mixed solution.

(2) It soaked manganese dioxide membrane (diameter 3 cm ar

径3 cm、厚さ1 mm) を前記(1)の原料低分子混合液中に浸し、二酸化マンガ膜中の微細な空隙中に(1)の原料低分子混合液を十分含浸させるため、真空デシケータ内で脱気した。30分後、二酸化マンガ膜からの発泡が認められなくなり、脱気が十分に行われたことを確認した。

【0035】(3) 二酸化マンガ膜を前記(1)の原料低分子混合液から引き揚げ、実施例1で用いたものと同じセル正極部に、二酸化マンガ膜面が正極集電板23上に来るようにセットした。脱脂綿で余分な原料低分子混合液を取り除いた後、前記(1)と同一組成の原料低分子混合液をマイクロシリンジによって所定量滴下し、正極表面上に所望の厚みの原料低分子液層を形成させた。本実施例では実施例1と同様に原料低分子液層の厚みを20  $\mu\text{m}$ とし、14  $\mu\text{l}$ の原料低分子混合液を二酸化マンガ膜上に滴下した。この状態において、セルの角ガスケット24と正極カバー22間からの原料低分子混合液の漏れは認められなかった。

【0036】(4) 前記(3)の二酸化マンガ/原料低分子混合液複合膜をセル正極部にセットされたままの状態、実施例1で用いたものと同じプラズマ重合装置内の基板ホルダーにセットする。基板ホルダーの下面には約5℃の冷却水を配管により循環させて、プラズマによる基板ホルダーの温度上昇に伴う原料低分子混合液の蒸発を防いだ。次に、アルゴンガスを10  $\text{cm}^3/\text{min}$  (at 25℃, 1 atm) の流量で流しながら真空層内を圧力2 Torrまで排気後、周波数10 kHz、放電電力7 W (放電電極上の電流密度:  $1.5 \times 10^{-4} \text{ A}/\text{cm}^2$ ) で2時間プラズマ重合させた。放電終了後、真空槽内を窒素ガスで大気圧まで戻し、セル正極部を取り出した。

【0037】(5) 得られた複合膜のプラズマ重合部分は柔軟な固体膜であり、セル正極部を傾けても複合膜からの液状物質の流れだしや変形は認められなかった。また、赤外吸収分光法により重合膜の化学構造を評価したところ、原料低分子のエチレンオキッド構造が保持され

d thickness 1 mm) which is provided with chemical polymerization method in starting material low molecular weight mixed solution of aforementioned (1), in order fully to impregnate starting material low molecular weight mixed solution of (1) in microscopic void in manganese dioxide membrane, outgassing it did inside the vacuum dessicator. After 30 min, foaming from manganese dioxide membrane stopped being recognized, you verified that outgassing was done in fully

[0035] (3) It pulled manganese dioxide film from starting material low molecular weight mixed solution of aforementioned (1) and dried, in order in same cell positive electrode part as those which are used with Working Example 1, for the manganese dioxide film surface to come on positive electrode collector sheet 23, it set. After removing excess starting material low molecular weight mixed solution with absorbent cotton, description above (1) with the starting material low molecular weight mixed solution of same composition predetermined amount was dripped with microsyringe, starting material low molecular weight liquid layer of the desired thickness was formed on positive electrode surface. With this working example thickness of starting material low molecular weight liquid layer was designated as 20  $\mu\text{m}$  in the same way as Working Example 1, starting material low molecular weight mixed solution of 14  $\mu\text{l}$  was dripped on the manganese dioxide film. In this state, angular gasket 24 of cell and a leak of starting material low molecular weight mixed solution from between positive electrode cover 22 were not recognized.

[0036] (4) Manganese dioxide / starting material low molecular weight mixed solution composite membrane of aforementioned (3) with state while it is set to the cell positive electrode part, is set to substrate holder inside same plasma polymerization equipment as those which are used with Working Example 1. It prevented evaporation of starting material low molecular weight mixed solution which circulating due to the pipe, accompanies cooling water of approximately 5℃ temperature rise of the substrate holder due to plasma in bottom surface of substrate holder. While next, letting flow argon gas with flow of 10  $\text{cm}^3/\text{min}$  (at 25℃, 1 atm), inside the vacuum layer to pressure 2 Torr after exhaust, 2 hours plasma polymerization it did with the frequency 10 kHz and discharge power 7 W (current density:  $1.5 \times 10^{-4} \text{ A}/\text{cm}^2$  on discharge electrode). After discharge ending and inside vacuum chamber you reset to atmospheric pressure with nitrogen gas, removed cell positive electrode part.

[0037] (5) Plasma polymerization portion of composite membrane which it acquires it was a flexible solid membrane, cell positive electrode part tilted and liquid substance from composite membrane started flowing and deformation was not recognized. In addition, when chemical structure of

ていることを確認した。窒素ガス雰囲気グローブボックス中で、セル正極部にセットされた複合膜上にリチウム箔（直径1 cm、厚さ0.3 mm）及びセル負極部を重ね、電池セルを構成した。セル内の複合膜及びリチウム箔はセル正極部とセル負極部をボルトとナットにより結合することによって外気からシールされる。セル正極部及び負極部に端子（25及び29）を取り付けて外部とセル内の導通を取り、充放電特性を評価したところ、電流密度0.02 mA/cm<sup>2</sup>の充放電サイクルで開放端電圧は3.4 Vであり、電池として機能することを確認した。

[0038]

【発明の効果】本発明により重合開始剤や架橋剤など第3成分の添加によらない清浄な雰囲気下で、均一な導電材料／高分子固体電解質複合膜を作製することができる。本発明ではリチウム支持電解質を成膜前に原料低分子中に溶解させるため、高分子固体電解質膜中の塩の分布は均一であり、塩濃度の制御も容易である。また、高分子固体電解質の原料低分子を導電材料中に浸透させて重合させているため、導電材料と高分子固体電解質間で良好な電気的・機械的接触が得られる。実施例で用いたポリアニリンや二酸化マンガンのリチウム電池の正極材料上に本発明による高分子固体電解質膜を複合化させることにより、軽量・コンパクトな全固体型リチウム電池を得ることが可能である。また導電材料としてエレクトロクロミズムを示す材料（例えば、ポリピロール、ポリチオフェン等の導電性高分子や三酸化タングステン等）を使用することにより、薄型の全固体型エレクトロクロミック素子の製造も可能である。

【図面の簡単な説明】

【図1】実施例で使用したプラズマ重合装置の構成図。

【図2】実施例において導電材料／高分子固体電解質複合膜の作製及び評価に使用した評価セルの構成図。

polymer film is appraised with infrared absorption spectroscopy, you verified that ethylene oxide structure of starting material low molecular weight is kept. In glovebox which is made nitrogen gas atmosphere, lithium foil (diameter 1 cm and thickness 0.3 mm) and cell negative electrode part were repeated on composite membrane which is set to cell positive electrode part, battery cell was formed. composite membrane and lithium foil inside cell seal are done from the external air by connecting cell positive electrode part and cell negative electrode part with bolt and nut. Installing terminal (25 and 29) in cell positive electrode part, and negative electrode part you took continuity inside outside and cell, when charge-discharge characteristic is appraised, release end voltage was 3.4V with charge-discharge cycle of current density 0.02 mA/cm<sup>2</sup>, you verified that it functions as battery.

[0038]

[Effects of the Invention] Under clean atmosphere which does not depend on addition of third component such as polymerization initiator and crosslinking agent with this invention, uniform electrically conductive material / polymeric solid electrolyte composite membrane can be produced. In order with this invention lithium supporting electrolyte before film formation to melt in the starting material low molecular weight, distribution of salt in polymeric solid electrolyte film is uniform, also control of salt concentration is easy. In addition, because starting material low molecular weight of polymeric solid electrolyte permeating in electrically conductive material, you polymerize, satisfactory electrical \* mechanical contact is acquired between the electrically conductive material and polymeric solid electrolyte. It is possible to obtain light weight \* compact completely solid type lithium battery, by composite making doing polymeric solid electrolyte film due to this invention on anode material of polyaniline and manganese dioxide or other lithium battery which are used with Working Example. In addition also production of completely solid type electrochromic element of thin form is possible by using material (Such as for example polypyrrole, polythiophene or other conductive polymer and tungsten trioxide) which shows electrochromism as electrically conductive material.

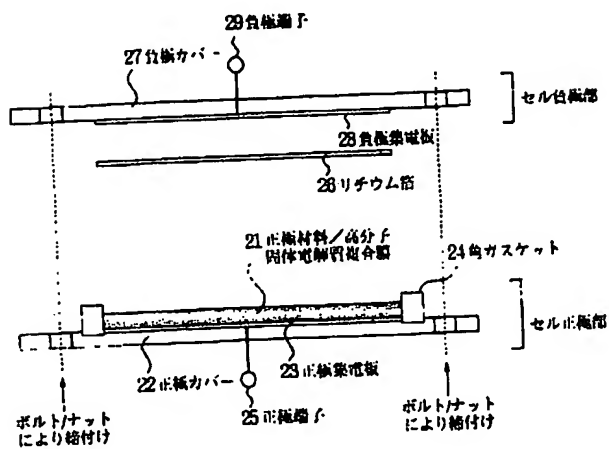
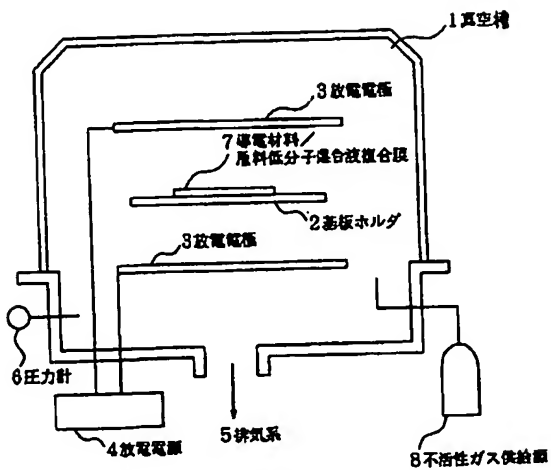
[Brief Explanation of the Drawing(s)]

[Figure 1] Configuration diagram of plasma polymerization equipment which is used with Working Example.

[Figure 2] Configuration diagram of test cell which is used for production and appraisal of electrically conductive material / polymeric solid electrolyte composite membrane in Working Example.

【図 1】

[Figure 1]



【図 2】

[Figure 2]

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